

A Study of the Relationship Between Anthropogenic Sulfate and Cloud Drop Nucleation

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A STUDY OF THE RELATIONSHIP BETWEEN ANTHROPOGENIC SULFATE AND CLOUD DROP NUCLEATION

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1. INTRODUCTION

The characteristics of the cloud drop size distribution near cloud base are initially determined by the aerosol particles that serve as CCN and by the local updraft velocity (Chuang et al., 1992). Chemical reactions of the emitted gaseous sulfur compounds due to human activities will alter, through gas-to-particle conversion, the aerosol size distribution, total number, and its chemical composition. Recently, Boucher and Rodhe (1994) and Jones et al. (1994) have each developed parameterizations relating cloud drop concentration to sulfate mass or aerosol number concentration, respectively, and used them to develop estimates of the indirect forcing by anthropogenic sulfate aerosols. These parameterizations made use of measured relationships in continental and maritime clouds. However, these relationships are inherently noisy, yielding more than a factor of 2 variation in cloud drop concentration for a given aerosol number (or for a given sulfate mass) concentration. The large spatial and temporal variabilities in the concentration, chemical characteristics, and size distribution of aerosols have made it difficult to develop such a parameterization from data.

In this paper, our focus is to develop a means for relating the predicted anthropogenic sulfate mass to cloud drop number concentration over the range of expected conditions associated with continental and marine aerosols. We start with an assumed pre-existing particle size distribution and develop an approximation of the altered distribution after addition of anthropogenic sulfate. We thereby develop a conservative estimate of the possible change in cloud drop number concentration due to anthropogenic sulfate.

2. ESTIMATE THE ANTHROPOGENIC SULFATE-CONTAINING AEROSOL SIZE DISTRIBUTION

The size distribution of anthropogenic sulfate-containing aerosols depends on the processes which form particulate sulfate. It is thought that H_2SO_4 is mainly formed during the aqueous conversion of SO_2 to SO_4^{2-} in cloud drops. H_2SO_4 is also formed in the gas phase where it may either condense onto pre-existing particles causing them to grow or form new particles through homogeneous nucleation. Homogeneous nucleation takes place only under special conditions of high sulfuric acid vapor pressure, high relative humidity, and low pre-existing particle surface area (Hoppel and Frick, 1990; Hegg et al., 1990; Kreidenweis et al., 1991; Clarke, 1993). Here, we neglect homogeneous nucleation in determining the aerosol size distribution in order to develop a lower limit to the prediction of new CCN.

Measurements which relate sulfate mass and aerosol number distributions are nearly non-existent, though measurements of sulfate mass and mass distribution do exist. Hence, we estimate number distribution of anthropogenic sulfate-containing aerosols based on the total aerosol number concentration and the amount of anthropogenic sulfate. We begin with an assumed pre-existing particle distribution which can be expressed as the superposition of three log-normal functions,

$$\frac{dN/N_{\text{total}}}{d \log d} = \sum_{i=1}^3 \frac{N_i}{\sqrt{2\pi} \log \sigma_i} \exp \left\{ - \frac{\left[\log \left(\frac{d}{D_i} \right) \right]^2}{2 \log \sigma_i^2} \right\} \quad (1)$$

The assumed size distribution parameters for continental and marine pre-existing aerosols are listed in Table 1. The origin and nature of the pre-existing aerosols are not treated here. The main issue here is how the size distribution of pre-existing particles will change after deposition of a given amount of anthropogenic sulfate.

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Table 1. Size distribution parameters for the pre-existing particles

	N_i	D_i (μm)	$\log \sigma_i$
Continental	0.548	0.025	0.25
	0.450	0.060	0.30
	0.002	0.750	0.35
Marine	0.450	0.030	0.20
	0.540	0.150	0.15
	0.010	0.500	0.15

The evolution of the pre-existing aerosol size distribution is primarily determined by two processes: growth by condensation of sulfuric acid vapor from OH oxidation of SO_2 and growth by in-cloud oxidation of SO_2 onto particles large enough to act as CCN followed by drop evaporation. For condensation of sulfuric acid vapor, the volume increase for a particle with radius r is taken to be proportional to the product of $rD(r)$, where $D(r)$ is the effective diffusion coefficient given by

$$D(r) = D \left[\frac{r}{r + \lambda} + \frac{4D}{r\nu} \right]^{-1} \quad (2)$$

and D is the diffusion coefficient for sulfuric acid vapor, λ is the mean free path, and ν is the mean thermal velocity (Hoppel et al., 1990). For in-cloud oxidation of SO_2 , the cloud drops are assumed to be monodisperse and convert the same amount of sulfate regardless of the original size of its CCN (Lelieveld and Heintzenberg, 1992). Langner and Rodhe (1991) estimated that the amount of sulfate transformed by OH oxidation is 19% - 55% of that by in-cloud oxidation. Thus, if sulfate is produced by these two pathways only, 65% - 85% of sulfate would be transformed by in-cloud oxidation of SO_2 ; a mean value of 75% is adopted in this work. The minimum radius of CCN is chosen in the range 0.05 - 0.20 μm (Lelieveld and Heintzenberg, 1992). We also assume that H_2SO_4 in particulate phase is completely neutralized by reacting with NH_3 and exists as $(\text{NH}_4)_2\text{SO}_4$.

Examples of the simulated anthropogenic sulfate-containing aerosol size distributions are shown in Fig. 1. Figure 1a shows the number distribution of continental aerosols before and after the deposition of anthropogenic sulfate. Also shown for comparison is the average continental aerosol distribution measured near the coast of Charleston, South Carolina (curve 1 of Fig. 7 in Hoppel et al., 1990). The simulated size distribution is plotted versus particle equilibrium size at a relative humidity 40% to be consistent with measured data (private communication). For this comparison, the anthropogenic and natural sulfate mass were assumed

to be 5 and 0.1 $\mu\text{g m}^{-3}$, respectively, consistent with the calculated annual average near Charleston (Penner et al., 1994), while the pre-existing aerosol number concentration was assumed to be 5500 cm^{-3} in keeping with that measured by Hoppel et al. (1990). Figure 1b presents the simulated marine aerosol number distribution as well as the average measured data over the remote tropical Atlantic ocean from Hoppel et al. (curve 4 of Fig. 7, 1990). The total aerosol concentration was assumed to be 250 cm^{-3} , the anthropogenic sulfate concentration deposited on the pre-existing aerosols was assumed to be 0.5 $\mu\text{g m}^{-3}$, and the natural sulfate was taken to be 0.3 $\mu\text{g m}^{-3}$. It is noted that condensational growth has a considerable effect on small particles, while in-cloud oxidation of SO_2 followed by cloud evaporation can change the pre-existing CCN size distribution. Good agreement between simulated number distributions with measurements indicates that the parameters listed in Table 1 may represent a reasonable "average" distribution for pre-existing particles.

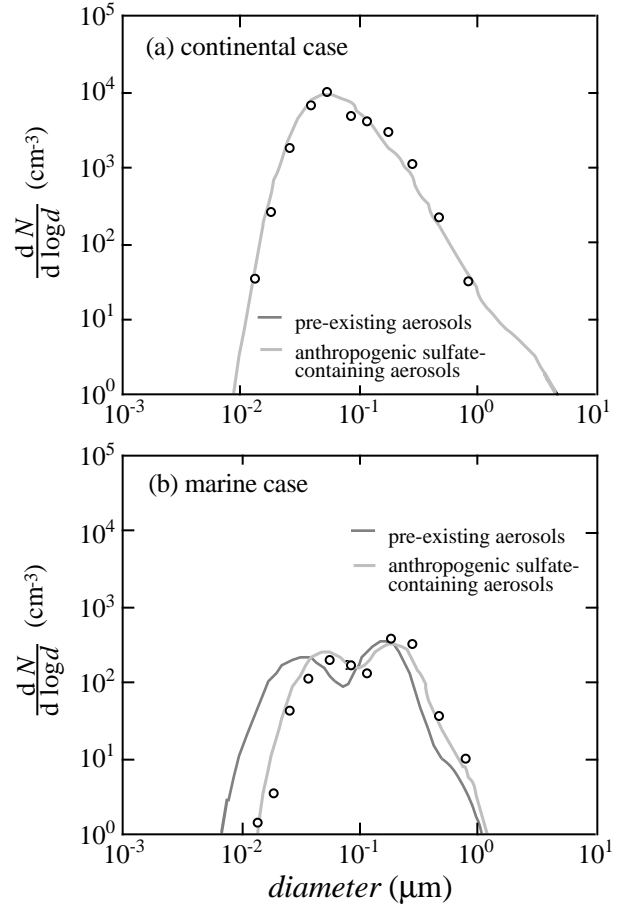


Figure 1. Simulated anthropogenic sulfate-containing aerosol size distributions. The open circles show measurements by Hoppel et al. (1990).

3. CLOUD DROP NUCLEATION AND PARAMETERIZATION

An aerosol particle becomes activated as a CCN when the environmental supersaturation ratio becomes greater than its critical value. The resulting drop grows to a size much larger than the initial size of the particle due to condensation of water vapor. The detailed microphysical model described by Chuang et al. (1992) was used to examine the consequence of water vapor diffusion to aerosols which are an internal mixture of sulfate and other materials. This model describes a Lagrangian air parcel which may also entrain environmental air. Here, we assumed the parcel dynamics were adiabatic because we are interested only in the initial stages of cloud development. Figure 2 presents the relationship of the predicted cloud drop number nucleated to anthropogenic sulfate in particles. In these calculations, we vary aerosol number concentration from 500 - 10000 cm^{-3} for continental case and from 50 - 500 cm^{-3} for marine case to cover the spatial and temporal variations expected for the concentration of pre-existing aerosols. We also

consider updraft velocities ranging from 10 cm s^{-1} to 200 cm s^{-1} to cover a wide range of updrafts expected in both stratus and stratocumulus. Looking at any one curve in Fig. 2, one notes that under many circumstances the predicted cloud drop number concentration is larger on particle size distributions with a higher loading of anthropogenic sulfate even though the total number of aerosol particles is unchanged in these simulations. The concentration of cloud drops is of course also affected by both updraft velocity and total (in this case pre-existing) aerosol number. For the continental case with a moderate updraft velocity 50 cm s^{-1} and aerosol number 2000 cm^{-3} , we estimate that the number of the condensationally-produced cloud drops would increase from 350 to 560 if a typical amount of anthropogenic sulfate 2 $\mu\text{g m}^{-3}$ in non-urban regions were added onto the pre-existing particles. For the marine case with the same updraft velocity but much lower aerosol concentration 100 cm^{-3} , the number of cloud drops nucleated would increase from 60 to 75 for a total deposition of anthropogenic sulfate equal to 0.2 $\mu\text{g m}^{-3}$.

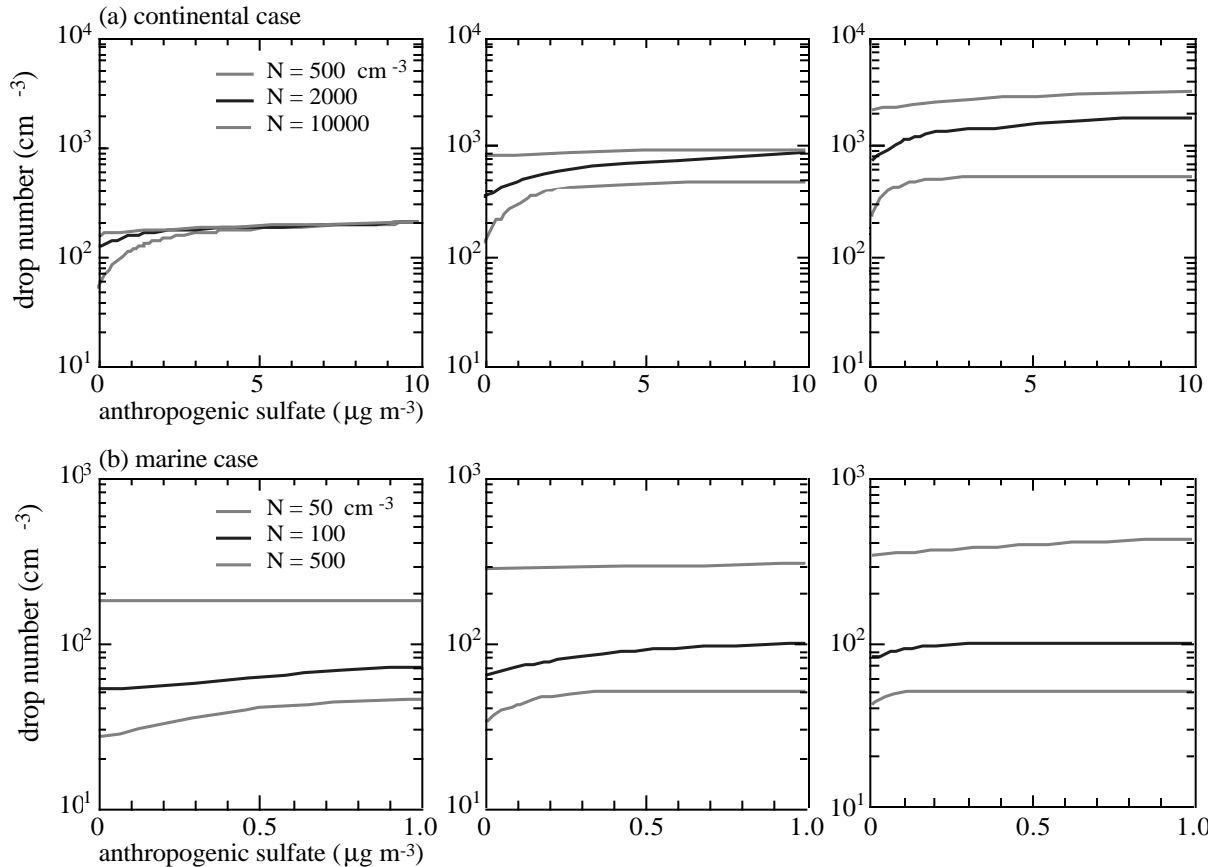


Figure 2. Predicted cloud drop number nucleated versus anthropogenic sulfate for updraft velocities 10 cm/s (left panel), 50 cm/s (middle panel), and 200 cm/s (right panel).

Figure 2 indicates that the anthropogenic sulfate has a significant influence on cloud drop concentration. Here, we parameterize the nucleation of cloud drops onto anthropogenic sulfate-containing aerosols based on the results from a detailed microphysical model. The cloud drop number nucleated (in cm^{-3}) is expressed in the form $N_d = w N_a / (w + c N_a)$ as suggested by Ghan et al. (1993), where N_a (cm^{-3}) is the pre-existing aerosol number concentration, and w is the updraft velocity in cm s^{-1} . c is expressed as follows

$$\text{over land: } c = 0.03659 + 22.739 X_L \quad (4)$$

$$\text{over ocean: } c = 0.03643 - 0.3616 X_O + 3.5767 X_O^2 \quad (5)$$

where $X_L = \log w [1 - \log w (.5 + \gamma) / \log N_a^2] / \log N_a^{5+\gamma}$, and $X_O = \log w [1 - \log w (.5 + 2\gamma) / \log N_a^2] / \log N_a^{2+1\gamma}$. γ is referred to as the shape parameter and is defined as the ratio of anthropogenic sulfate loading (in $\mu\text{g m}^{-3}$) to the total aerosol number (in 1000 cm^{-3}). Scatter diagrams of the cloud drop concentrations predicted from the parameterization versus the simulated values from the microphysical model are shown in Fig. 3. Since the scatter in these figures is small, we expect that the use of this parameterization should be adequate to estimate the effect of anthropogenic sulfate-containing aerosols on initial cloud drop number concentrations.

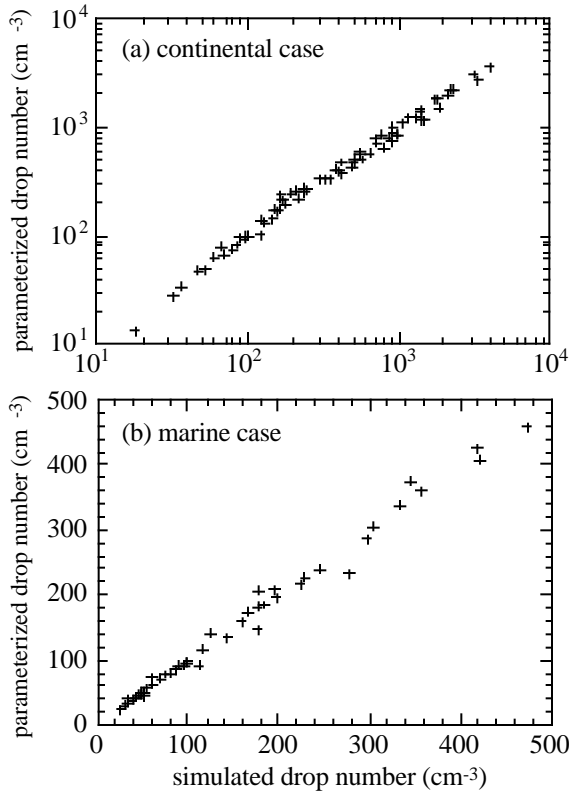


Figure 3. Cloud drop number concentrations from the parameterization versus the simulated values.

4. CONCLUSIONS

We investigated the relationship between anthropogenic sulfate-containing aerosols and the condensationally produced cloud drops. The changes in aerosol size distribution associated with anthropogenic sulfur emissions may increase the number of cloud drops with subsequent influence on cloud albedo and climate. It has been suggested that the increase in CCN in industrial regions might explain why the Northern Hemisphere has not been warming as rapidly as the Southern Hemisphere over the last 50 years (Wigley, 1989).

In reality, the aerosol size distribution is the result of processes working simultaneously and continuously with such sources as sulfur, soot, particulate organic carbon, nitrate, ammonium, etc. Instead of applying a complete aerosol model to investigate the effect of anthropogenic sulfur emissions on the aerosol size distribution, we simply derived the anthropogenic sulfate-containing aerosol distribution by assuming that 75% of the anthropogenic sulfate was formed through aqueous-phase oxidation and the remaining 25% condensed onto a prescribed pre-existing particle distribution. Uncertainties may arise from the assumed fraction of sulfate produced by condensation and in-cloud oxidation. In addition, new particle formation through homogeneous nucleation of $\text{H}_2\text{SO}_4/\text{H}_2\text{O}$ is ignored in this paper; however, it could be important in the upper troposphere where surface area of existing particles is relatively low (Clarke, 1993) or in regions recently scavenged by cloud (Hoppel and Frick, 1990) or in the proximity of clouds (Hegg et al., 1990). Uncertainties can also arise from the assumed “pre-existing particle size distribution” which must result from a variety of processes (e.g., homogeneous nucleation, condensation, coagulation, dry and wet deposition) and sources involving the entire suite of aerosol types (Penner et al., 1994). The prescribed pre-existing size distribution was chosen to represent an “average” particle distribution where no anthropogenic sulfate was present. Although it may remain questionable whether the pre-existing distribution is independent of anthropogenic sulfate and can be treated separately, we believe that the approach used in this study provides a useful first attempt to quantify the relationship between anthropogenic sulfate and cloud drop nucleation.

In future work, we will apply the results from this study to parameterize the number concentration of cloud drops in a climate model to improve the assessment of the anthropogenic sulfate-containing aerosol indirect effects on the global radiation budget.

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